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DIFFERENTIAL HEAT OF SORPTION OF VAPOR ON ACTIVE CHARCOAL.

II. Result of Measurement.

By KAZUO SATO.

Substances Employed.

Active Charcoals.

a) Phosphoric acid activated charcoal (P-Charcoal).

Saw dust of the American hemlock tree was digested with the solution of phosphoric acid and sulphuric acid at the boiling point for several hours. After filtering the mixture, cake was grinded, given a form of cylinder and then heated up to a temperature of about 800° . The product is cylindrical, 2 mm in diameter and 2.5 mm in height.

b) "Norit" charcoal (N-Charcoal).

The so-called "Norit, standard", made in Holland, being activated with steam. Cylindrical, of 2 mm diameter and 3 mm height.

c) Sodium sulphate activated charcoal (S-Charcoal).

Saw dust of the Western red cedar was digested with a solution of sodium sulphate and sulphuric acid, and then treated similarly as the P-charcoal. Activation temperature was about 730° . Cylindrical, of 2.5 mm diameter and 3 mm height.

Before use charcoals were boiled with dilute hydrochloric acid, washed with boiling water and then dried at 140° . It is regarded that charcoal becomes free from any impurities when heated up to 900° and evacuated in high vacuum for several hours. The state was decided as the starting point of our measurement.

Adsorptives.

a) C_2H_5OH Merck's anhydrous reagent, dehydrated with Ca, and distilled in vacuum three times.

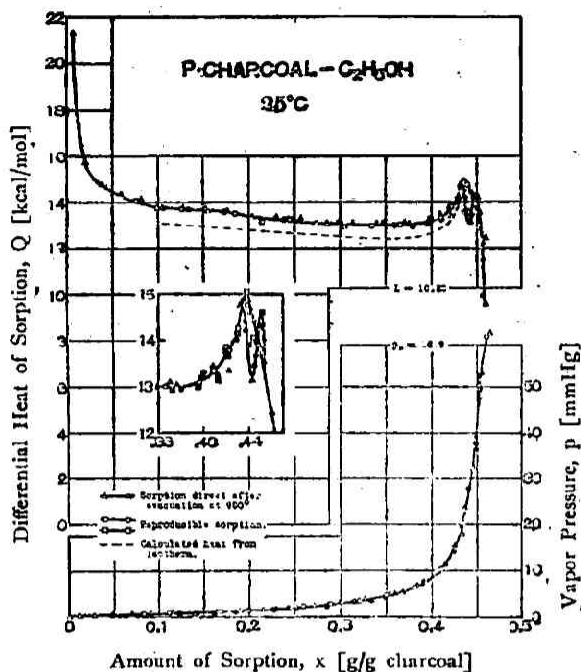
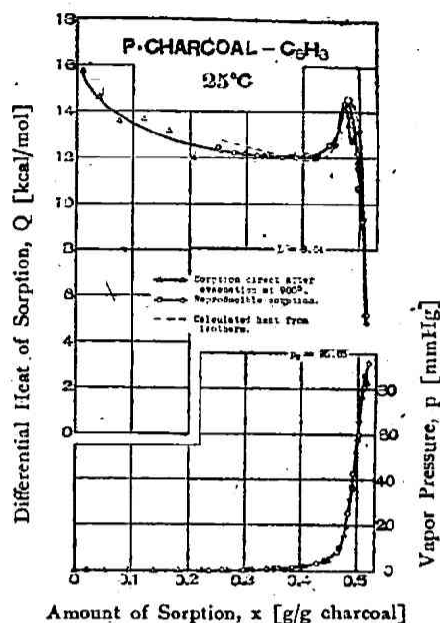
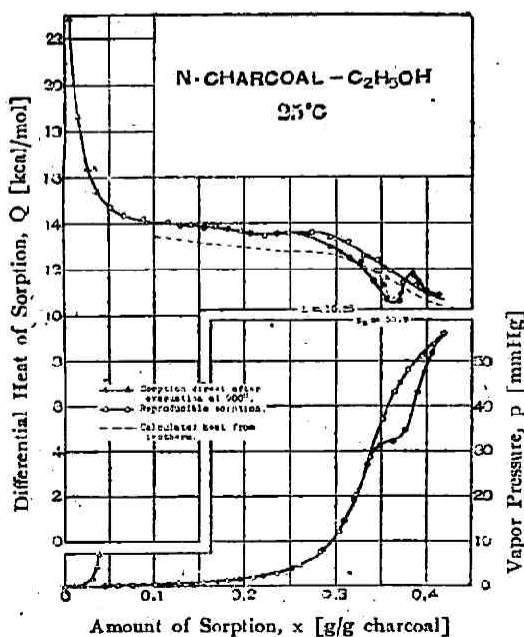
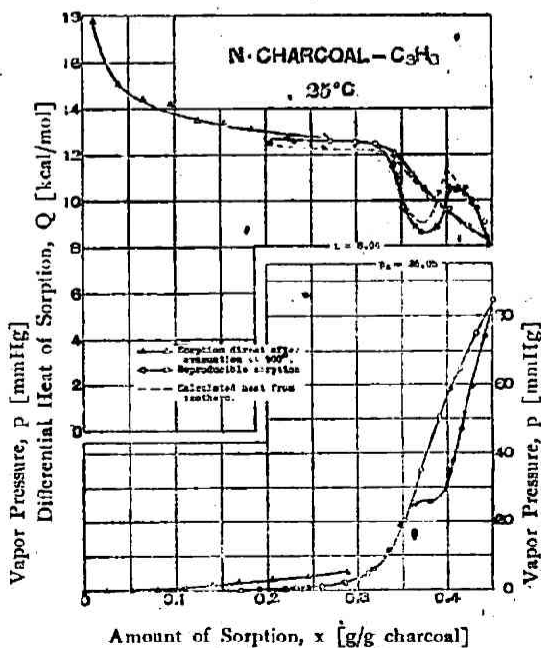
b) C_6H_6 Kahlbaum's reagent for molecular weight determination, purified several times by solidification, then distilled in vacuum.

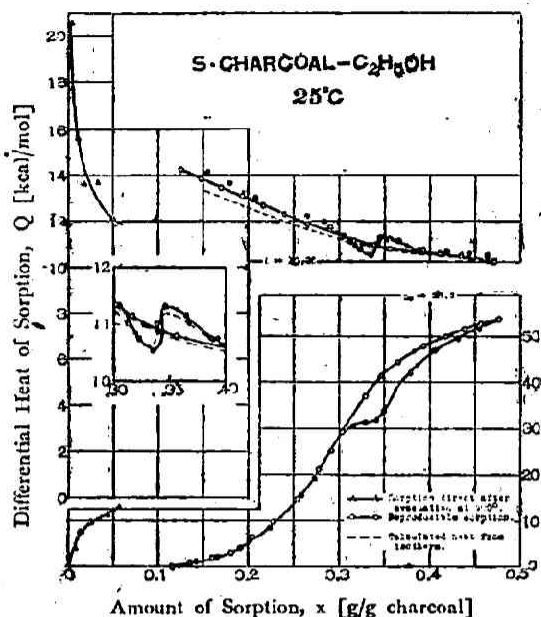
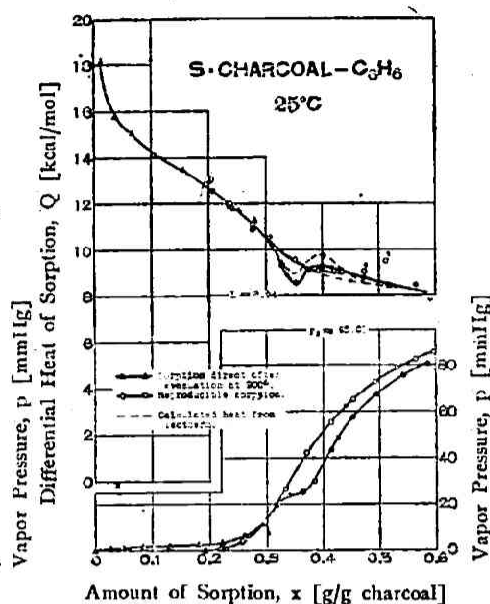
Results of the Measurement.

The results of the measurement of sorption isotherm and the differential heat of sorption are summarized in Figs, 3~8.

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Fig. 3. P-Charcoal- C_2H_5OH .Fig. 4. P-Charcoal- C_6H_6 .Fig. 5. N-Charcoal- C_2H_5OH .Fig. 6. N-Charcoal- C_6H_6 .

Fig. 7. S-Charcoal- C_2H_5OH .Fig. 8. S-Charcoal- C_6H_6 .

Unreproducible and reproducible sorption.

The final vapor pressures of the first sorption process directly after the desorption at 900° are extraordinarily high, and more or less non-condensable gases are found in the gaseous phase. Evacuating again and then introducing vapor once more, the final pressure rides on the different curve from the first, that is, the sorption process is considered unreproducible, and not in a real sorption equilibrium. But while repeating the adsorption and desorption of vapor on charcoal, the final pressure gradually falls to the curve which is now completely reproducible. We call the former case "unreproducible sorption" and the latter "reproducible sorption". It is regarded that in the unreproducible process the molecules of the gas attaching on charcoal, not being detached even at 900° and high vacua because of being packed in narrow space, are substituted step by step by the molecules of vapor. These substituted vapor molecules can not be desorbed by evacuation at a low temperature of 25° , and remain as "residual sorption amount". Accordingly, the starting point of the curve of reproducible sorption is higher by residual amount than that of the unreproducible sorption curve.

Hysteresis of sorption.

In the reproducible sorption isotherm near the saturated vapor pressure, there is a portion of different values of equilibrium pressure between the adsorption and desorption processes, drawing a loop. This is not an abnormal curve as in the

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case of the unreproducible sorption, but can be accurately reproduced again and again.

Differential heat of sorption.

The curve of the differential heat of sorption for every combination of active charcoals and vapors is distinguishable in four parts. The differential heat of sorption on bare charcoal is very high, amounting to about 20 [kcal/mol], followed by steeply decreasing curve. In the reproducible sorption process, the curve indicates increasing tendency again, sometimes distinct maximum, and finally goes down directly towards the heat of condensation of the vapor. In the desorption process, corresponding to the hysteresis in isotherm, the curve pursues different course from the adsorption process, and at the base of hysteresis curve it approaches again to the heat of condensation indicating a distinct minimum.

Consideration on the Observed Differential Heat.**Unreproducible sorption.**

The first and the succeeding sorptions on bare charcoal are regarded as an activated and the van der Waals adsorptions judging from the high and successive quickly decreasing values respectively of the heat of sorption as ordinarily seen in the case of adsorption of gases on solids.

Maximum and minimum in differential heat of sorption.

The results of the experiment show convincingly the existence of maximum and minimum in the curve of the differential heat of sorption of vapor on charcoal, and this is expected easily from the form of sorption isotherm in accordance with Polanyi's wetting theory.

Take the saturated vapor pressure at the temperature T [$^{\circ}\text{K}$] as p_s , the equilibrium vapor pressure at the sorbed amount x [g/g of charcoal] as p_x , and the affinity of wetting in the state, A_x [kcal/mol of vapor], defined by Polanyi¹⁾ will be as follows:

$$A_x = RT \ln \frac{p_s}{p_x} \dots \dots \dots (1)$$

As the latent heat of condensation, L [kcal/mol], and differential heat of sorption, Q_x [kcal/mol], of vapor at the temperature T are given respectively as below:

$$L = RT^2 \frac{d \ln p_s}{dT}, \quad Q_x = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_x \dots \dots \dots (2)$$

Q_x becomes from these quantities,

1) F. Goldmann u. M. Polanyi; *Z. physik. Chem.*, 132, 321 (1928).

$$Q_x = A_x + T \left(\frac{\partial A_x}{\partial x} \right)_T \left(\frac{\partial x}{\partial T} \right)_{A_x} + L \quad \dots\dots\dots (3)$$

Introducing the idea of Polanyi concerning on the sorption layer, this becomes also:

$$Q_x = A_x - a_{ads} x T \left(\frac{\partial A_x}{\partial x} \right)_T + L \quad \dots\dots\dots (4)$$

where a_{ads} is the thermal expansion coefficient of sorptive in the sorbed state, and putting this equal to that of the ordinary liquid state, a_l , we shall obtain the following equation as a conclusion for the differential heat of sorption at the state of sorbed amount x :

$$Q_x = A_x - a_l x T \left(\frac{\partial A_x}{\partial x} \right)_T + L \quad \dots\dots\dots (5)$$

With this equation we can calculate the differential heat of sorption along the course of sorption process from a sorption isotherm at only one temperature. The values thus calculated are indicated in the figures as dotted lines and are regarded as of fairly good coincidence within the scope of higher vapor pressures, especially in the positions of maximum and minimum of heat. A constant difference in the observed and the calculated values in the lower vapor pressure range, may be attributed to imperfect knowledge for the sorption layer in this range.

Equation (5) also can be rewritten as follows:

$$Q_x = A_x + a_l R T^2 \left(\frac{\partial \ln p}{\partial \ln x} \right)_T + L \quad \dots\dots\dots (6)$$

As A_x varies monotonously with x , the existence of maximum and minimum in differential heat depends entirely on the value of the term $(\partial \ln p / \partial \ln x)$ in equation (6), which is decided easily at a glance of the form of isotherm obtained at one temperature.

Capillary condensation.

Comparison of isotherm and differential heat curve for a sorption process indicates that the minimum of heat, approaching to the latent heat of condensation, is closely connected with the base of hysteresis loop of isotherm, and that the equilibrium vapor pressure of a sorptive at that point is common to all charcoals as seen in the relation between heat *versus* vapor pressure in Fig. 9. On the assumption of capillary condensation at that point, the radii of condensing pores were calculated with W. Thomson's formula from the vapor pressures corresponding to minimum heat, and being corrected by thickness of monomolecular wetting layer, the radius of capillary pore of about 20 Å was obtained, which is found to be also common to all cases as seen in Table I. This may mean that there is definite crevice, its radius of curvature is about 20 Å, in charcoals in spite of the method

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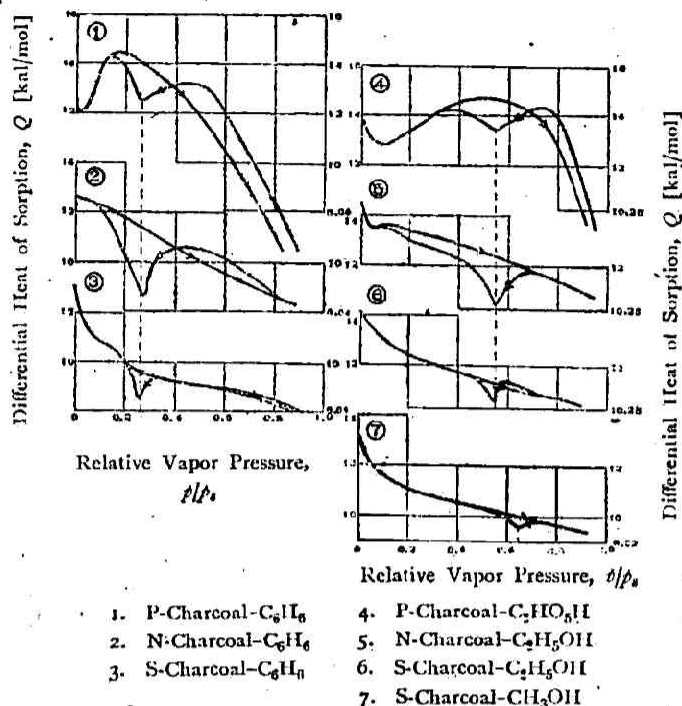


Fig. 9. Relation between Differential Heat and Equilibrium Vapor Pressure.

of activation, and any vapor of adsorptives presents here the phenomenon of capillary condensation.

Hysteresis.

The features of isotherm and differential heat curve for P-charcoal contrast with those for S-charcoal, and there can be found nothing in common among these charcoals. But inserting the curves for N-charcoal among them, it is found that the phenomenon is essentially the same among three sorts of charcoal, P- and S-charcoal are representatives of the extreme cases of a sorption mechanism. For instance, despite of no sign of hysteresis in the isotherm of P-charcoal, there is

Table 1. Calculation of Capillary Radius.

$$\ln \frac{p_s}{p} = \frac{2\sigma M}{r' \rho_l R T}$$

Sorbent	Relative vapor press. corresp. to min. of heat p/p_s	Radius of condensing pore r' [Å]	Thickness of mono-molec. layer inside the wall of pore d [Å]	Radius of capillary pore r [Å] ($=r'+d$)
CH_3OH	0.665	18.1	2.39	20.5
C_2H_5OH	0.544	16.8	3.67	20.5
C_6H_6	0.265	14.9	5.00	19.9

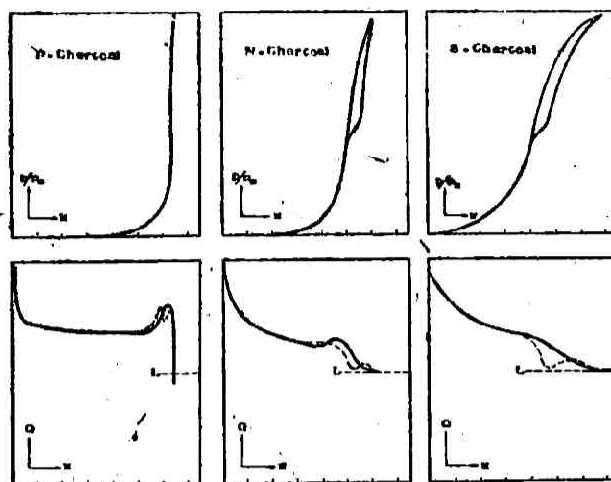


Fig. 10. Comparison of Isotherms and Differential Heat Curves for Various Charcoals.

seen a definite evidence of it in the curve of differential heat. Accordingly, it is understandable that the sorption of vapor on charcoal is usually accompanied by the phenomenon of hysteresis in all cases. The difference of appearance between charcoals may be attributed to that of the form of pores, resulting the difference of densities of charcoals as observed by the author. The densities of P- and S-charcoals were 0.928 and 0.716 respectively, the clear difference being noteworthy.

Summary.

1) The sorption isotherm and the differential heat of sorption of organic vapors on various active charcoals have been accurately measured at 25° over-all the processes of adsorption and desorption by means of an adiabatic calorimeter.

2) In the curve of the differential heat of sorption four steps of sorption process are distinguishable, i. e., an activated and the van der Waals sorptions respectively, wetting and capillary condensation.

3) The heat of sorption calculated from the isotherm according to the Polanyi's wetting theory almost coincides with the observed values in higher vapor pressures, and the maximum and minimum in differential heat of sorption have been confirmed to exist from the point of either experimental or theoretical views.

4) Phenomenon of capillary condensation of hysteresis, and pores of about 20 Å in radius of curvature have been justified to exist in any charcoals, regardless of the form of isotherm.

In conclusion, the author wishes to express his hearty gratitude to the late

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Prof. S. Tamaru for his kind guidance, to Prof. S. Horiba and Mr. N. Nagasako for their keen interest and constant encouragement throughout the investigation. Further, the author takes this occasion to express his thanks to Mr. S. Iwasaki for his assistance to construct the apparatus. The cost of this research has been defrayed from the subsidy from the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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